J. Phys. IV France **9** (1999)

OMVPE of GaN using $(N_3)_2Ga[(CH_2)_3N(CH_3)_2]$ (BAZIGA) in a cold wall reactor

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Abstract: Transparent ,smooth, epitaxial and stoichiometric films of GaN were grown on $Al_2O_3(0001)$ substrates at temperatures as low as 1070K with a growth rate of 2µm/hr using the title compound without any additional source of nitrogen (ammonia). The concentrations of the fragments $HGaN_x$ and GaN_x (x = 1 - 6) in the boundary layer as a function of temperature correlate with the growth rate (molecular beam sampling via pin hole, MS and REMPI-TOF spectroscopy) of the GaN films deposited. This indicates that tailored single source precursors offer a serious potential to grow films of group-13 nitrides significantly below 1300K.

1. INTRODUCTION

GaN is a direct, wide band gap semiconductor which has been intensively investigated over the last decade, and has achieved practical success in optoelectronic devices such as green/blue light emitting diodes and the blue laser [1-3]. In general the group-13 nitrides AlN, GaN and InN and their alloys find applications in various fields such as ultrahigh density optical storage systems, high temperature electronics etc., as these materials possess properties such as mechanical hardness, inertness and high thermal stability [4,5]. Device quality crystalline group-13 nitrides are conventionally grown by vapor phase epitaxy on single crystalline substrates which involves trialkyl derivatives of the group-13 metals and ammonia as reagents at high temperatures [6]. In case of GaN, substrate temperatures as high as 1000°C is employed as it is necessary, due to the high thermal stability of ammonia (15% pyrolysed at 950°C) [7]. This also leads to the problem of nitrogen effusion from the film, even though the ratio of ammonia flow rate to the alkyl source of gallium is as high as 2000 [8]. As a result, the films have a high background n-type carrier concentration, resulting in uncontrollable p-type doping [9]. The high temperatures involved also limits the choice of substrates and results in residual strains in the film grown.

The search for alternative sources is largely being driven by the idea that, with the use of single source precursors, having a pre-formed Ga-N bond, the substrate temperature can be reduced. Also the use of corrosive, toxic and pyrophoric properties of the classical precursors can be avoided. There has been reports in the recent past on the study of single source precursors such as $(Et_2GaN_3)_3$, $(Et_2GaNH_2)_3$ etc.[10,11]. Although these precursors have been successfully used to deposit GaN at low temperatures, the quality of the obtained material was poor and none of these precursors have been vigorously tested for any technical application. Our aim is to further develop single source precursors which would be non-pyrophoric, non-toxic, non-explosive, possessing a molecular structure with a metal-nitrogen bond and no or at least a few M-C, C-C, C-H, N-C of N-H bonds. Also to ensure stoichiometric growth, the precursor should be nitrogen rich and contain the nitrogen in an activated form for the crystal growth. We have reported earlier the use of intramolecularly stabilised azide based precursors as an alternative source for the CVD of group-13 nitrides [12,13]. In this paper we report, the growth and characterisation of epitaxial GaN using the single source precursor , Bisazido dimethylaminopropyl gallium, (BAZIGA) in a cold wall reactor at low temperatures. To probe the idea of the pre-formed Ga-N bonds in the precursor, in-situ investigation of the fragments arising near the boundary layer of the sapphire substrate due to the thermal decomposition of BAZIGA was undertaken. This was done using molecular beam quadrupole and REMPI-TOF (resonance enhanced multiphoton ionisation time of flight) mass spectrometry.

2. EXPERIMENTAL

The synthesis and characterisation of the intramolecularly stabilised organogallium azide $(N_3)_2Ga[(CH_2)_3NMe_2)]$, (BAZIGA) has been reported earlier[14]. The precursor is a liquid at room temperature (25°C) but colourless crystalline solid below room temperature and has been synthesised on a multi gram scale (~25g). Film depositions were carried out in a home built horizontal cold wall reactor (Fig.1).

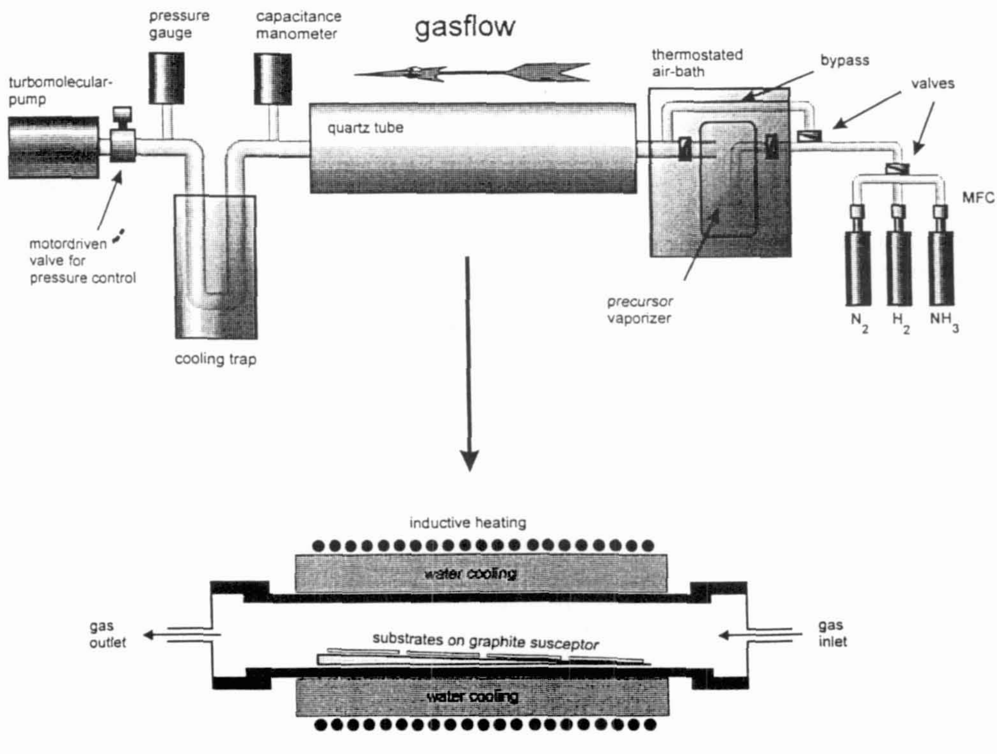

Fig. 1: Schematic diagram of the cold wall CVD reactor.

The CVD reactor was equipped with mass flow controllers, quartz tube, cooling trap to collect the by-products of the CVD reaction, turbomolecular pump to carry out film depositions at low pressures, a motor driven throttle valve to regulate the pressure during deposition. The precursor was stored in a glass vaporiser. Films were grown on single crystalline Al_2O_3 substrates (sapphire) placed on SiC coated graphite susceptors. The substrates were heated using an inductive heating arrangement. Prior to film deposition the substrates were cleaned with organic solvents and then etched in a mixture of hot H_2SO_4 / H_3PO_4 (3:1). Rinsed with de-ionised water and then subjected to a pre-treatment at 1300K for 30min in vacuo, followed by hydrogen annealing for 30min (10sccm) at the same temperature. The temperature was brought down to 1070K and then ammonia (25sccm) was used for nitridation of the substrate for 15min. After nitridation the substrate temperature was set to the desired value and film deposition was carried out by vaporising the precursor at 360K using nitrogen (40sccm) as the carrier gas. Typically 0.5-1.0 g of the precursor was used for a single deposition run which lasted for about one hour. The reactor pressure was of the order of 80 mbar during deposition. The films were characterised by a variety of techniques such as thickness measurements (profilometry), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), Rutherford back scattering (RBS) etc.

Identification of species from the gas phase in the layer close to the substrate was performed in a molecular beam sampling system consisting of three differentially pumped vacuum chambers (Fig.2).

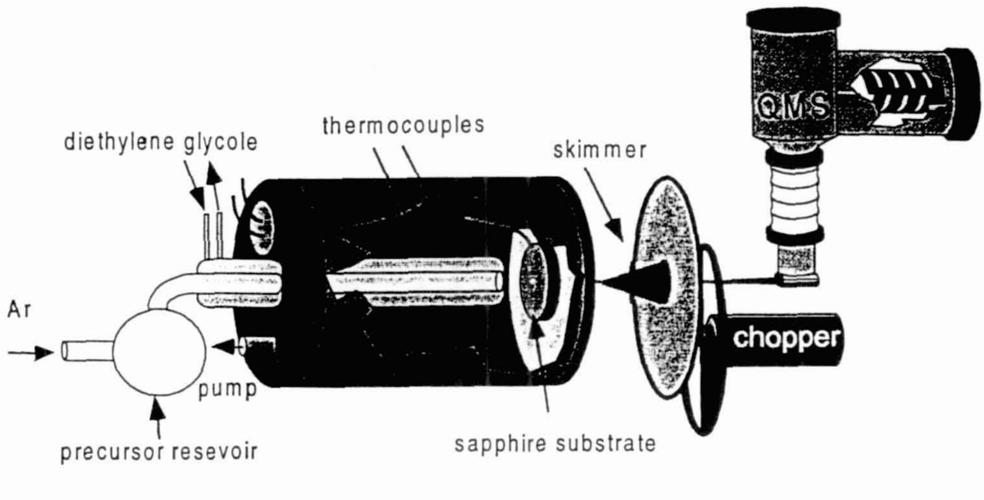

Fig.2: Molecular beam sampling with attached deposition chamber and quadrupole mass spectrometer for detection of species within the boundary layer through a pinhole (150μm in diameter) in the substrate.

The precursor reservoir and the vapor lines into the reactor (stainless steel tube) were made of quartz glass and were heated to about 380K during the experiments. BAZIGA decomposes exothermically above 540K to yield amorphous GaN. Argon was used as the carrier gas and for the calibration of the temperature dependent peak intensities. The main gas stream was pumped by a mechanical pump and through a small hole (300μm) in the c-plane sapphire substrate, a molecular beam was formed by species within the gas flow, which then passes into the next vacuum chamber. Subsequently, the beam enters through a skimmer into a third vacuum chamber to provide a low enough pressure necessary for mass spectrometry. Measurements of GaN_x and $HGaN_x$ were investigated by a quadrupole mass selector (Balzers QMS 311) with electron impact ionisation. Ions were extracted perpendicular to the molecular and electron beam. A mechanical chopper was used to discriminate between background gas in the vacuum chamber and species originating from the deposition chamber. Ga atoms were detected by REMPI-TOF as this type of spectroscopy gives in contrast to QMS a double reference of the species which have to be detected, first the wavelength of the resonant ionisation and second the mass of the species.

3. RESULTS AND DISCUSSION

Transparent and epitaxial films of GaN were obtained at temperatures as low as 1070K using the cold wall reactor on $Al_2O_3(0001)$ substrates. The film growth rates were of the order of 2μm/hr (profilometry and RBS measurements). Fig.3 shows the x-ray rocking curve analysis (002 plane) of the GaN film grown at 1070K. The FWHM was determined to be 0.72°.

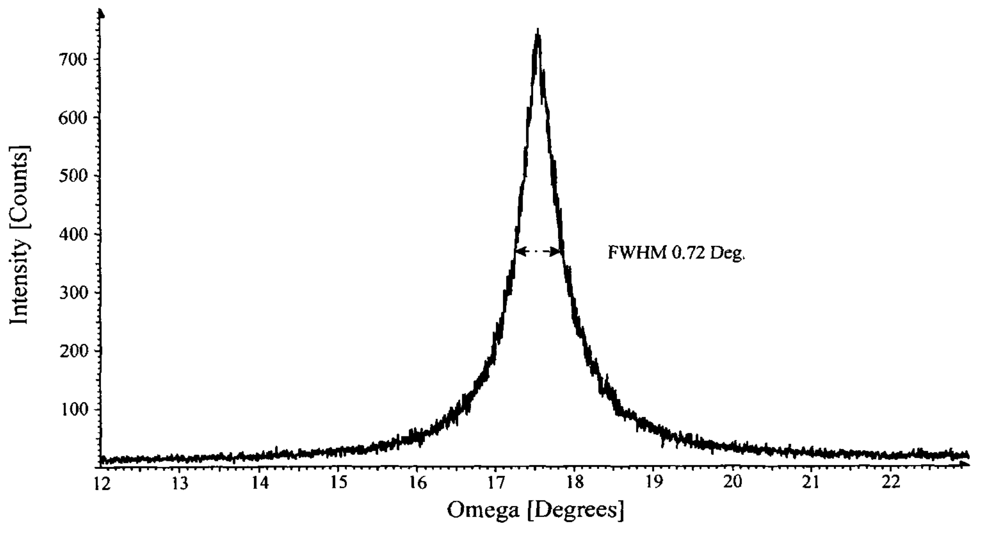

Fig.3: X-ray rocking curve of the (0002) reflection of GaN film on $Al_2O_3(0001)$ substrate deposited at 1070K.

Below 1070K the films were found to be polycrystalline. The composition of the film was analysed by RBS measurements and stoichiometric GaN (1:1, ±5%) was obtained. The morphology of the films were analysed by SEM and AFM and Fig.4 shows the surface morphology of the GaN film obtained by AFM. It is seen that broad pyramidal features are formed terminating into broad humps. Complete coverage of the sapphire substrate was achieved with a dense film having a rms roughness of about 16nm.

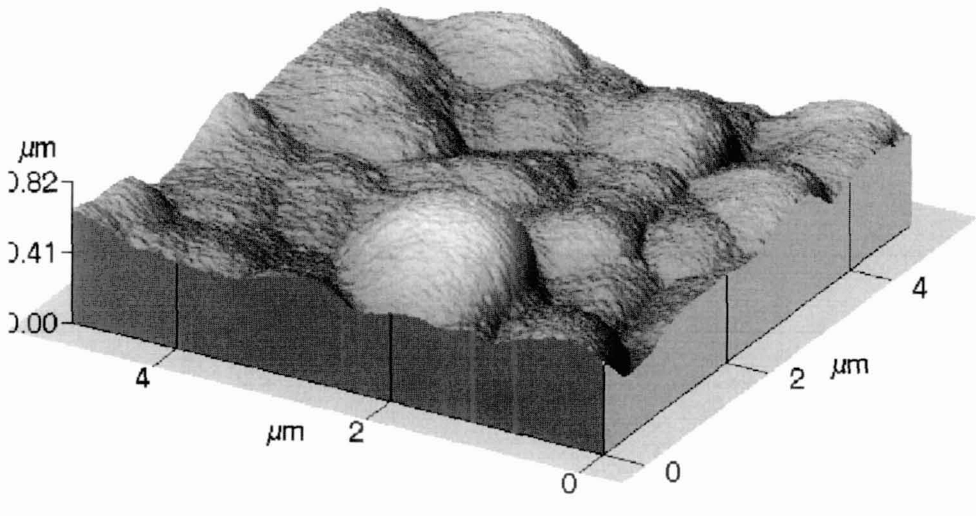

Fig.4: Atomic force microscopy image of GaN film grown on Al_2O_3(0001) substrate deposited at 1070K.

Fig.5 shows the mass spectrum of BAZIGA at a substrate temperature of 550K. The parent peak of the compound is clearly seen at a mass of 239 and 241 amu respectively. It is also seen from the fragmentation pattern that BAZIGA looses stepwise N-atoms depicted in mass 225(227), 211(213), 197(199), 183(185), 169(171) and 155(157) [the main isotopes of gallium are 60.4% Ga^{69} and 39.6% Ga^{71}]. It can also be seen from the intensity of the spectrum that total loss of a azide group (N_3) is favoured under the conditions of electron impact ionisation (20eV). It is important to investigate the species that arise by elimination of the organic donor (via breaking the Ga-C bond of β-elimination) and could be important in the growth of GaN layers. In the mass regime 154 ($HGaN_6$), 153(GaN_6), 98($HGaN_2$), 97(GaN_2) all possible hydrogen-gallium-nitrogen compounds received by the loss of the organic donor are detected (this is depicted in the insert of Fig.5) for the species $HGaN_2$ and GaN_2). The signals show exactly the relative isotopic abundance for gallium and as there are no organic compounds within the experiment at a mass between 87 and 250 amu, the signals can only arise from the above mentioned compounds. Therefore it can be surmised that BAZIGA thermally decomposes via β-elimination and direct Ga-C bond cleavage to give nitrogen rich gallium and hydrogen-gallium compounds. The dependence of growth rate of GaN on the nitrogen containing gallium compounds and gallium atoms with increasing substrate temperature was also investigated and this is shown in Fig.6 for $HGaN_x$ and GaN_x for x = 2 or 6 (signal intensity as a function of substrate temperature). Growth of GaN from BAZIGA resulted in amorphous layer with a growth rate of up to 10µm/hr in the temperature range 620-770K. At temperatures of around 900K, polycrystalline material was obtained with a growth rate of 4µm/hr.

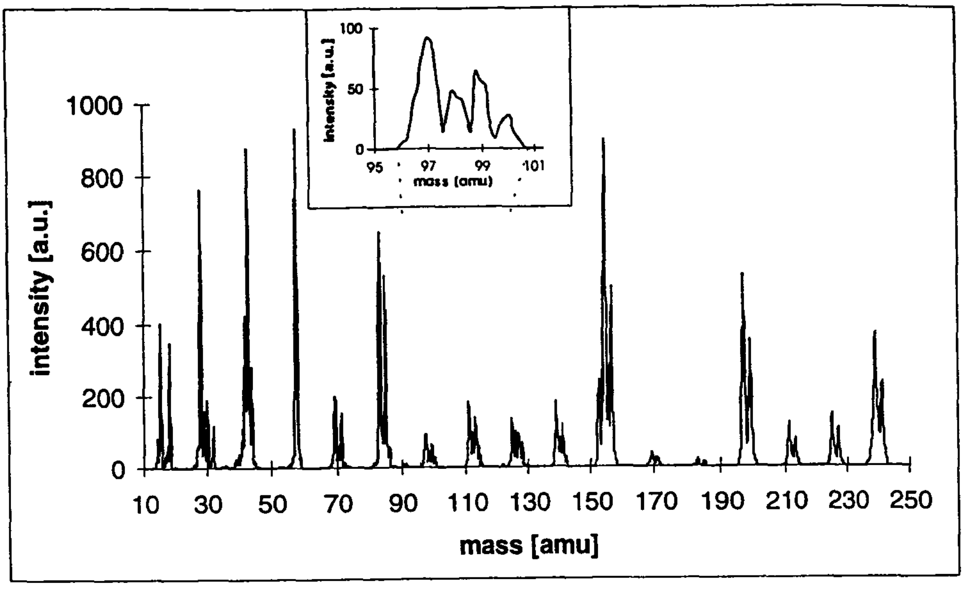

Fig.5: Quadrupole mass spectrum of fragments generated by electron impact ionisation of BAZIGA, $[(N_3)_2Ga[(CH_2)_3NMe_2]$.

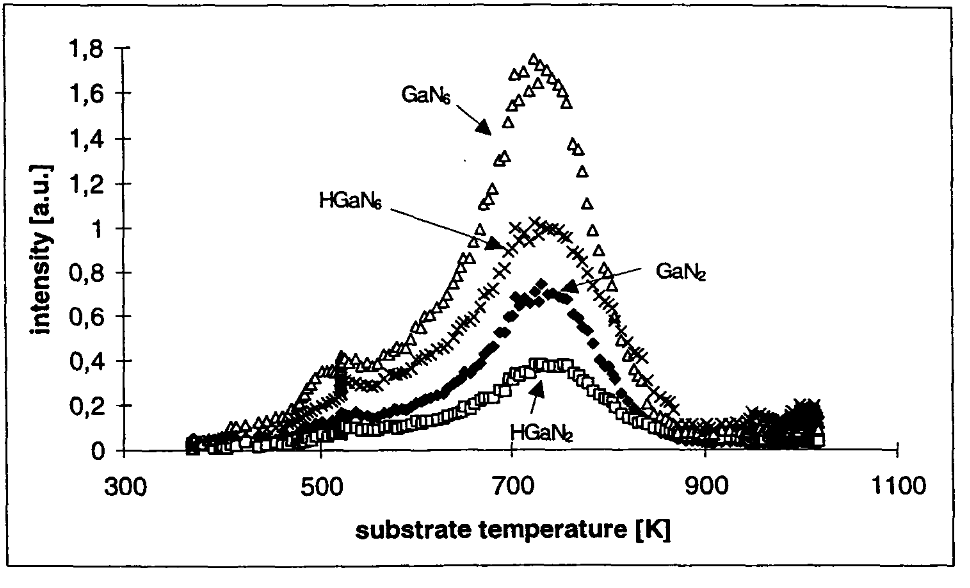

Fig.6: Variation of GaN_2, $HGaN_2$, GaN_6 and $HGaN_6$ mass signal as a function of substrate temperature.

The experimental set-up of the special reactor used for these studies did not allow the heating of the substrate above 900K. Maximum of H_yGaN_x (y = 0 or 1, x = 2 or 6) concentrations lead to corresponding maximum in deposition rate.Thus the concentration of the fragments $HGaN_x$ and GaN_x (x = 2-6) in the boundary layer as a function of temperature correlate with the growth rate.

4. SUMMARY AND CONCLUSIONS

The concept of nitrogen rich azide based organometallic compounds like BAZIGA can be a serious potential as a candidate for a new type of single source precursor for group-13 nitrides. BAZIGA serves as an effective source for the growth of epitaxial and stoichiometric GaN films at low temperatures without the need of any ammonia. The fragments such as $HGaN_2$, GaN_2, $HGaN_6$ and GaN_6 (in general nitrogen rich fragments) arise by the thermal decomposition of BAZIGA on a sapphire substrate. The maximum growth rate of GaN layers is achieved when a maximum of gallium-nitrogen fragments can be observed at a substrate temperature of 750K although amorphous GaN was obtained at this temperature. Further developments may be directed towards a precursor whose temperature dependence on the fragmentation, produces N-rich gallium species that match better the minimum temperature necessary for epitaxial growth at about 1000K.

Acknowledgement

Financial support by the Deutsche Forschungsgemeinshaft (DFG) is gratefully acknowledged. One of the authors AD would like to thank the Alexander von Humboldt Foundation, Germany for the fellowship.

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